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Project Title: Role of Protozoan Grazing in the Fate and Transport of particle reactive trace elements in the marine environment

### Goals

The goal was to determine the importance of protozoan grazing on the fate and transport of particle reactive elements, by studying the chemical transformations of particulate metals when ingested by protozoan grazers. These goals were established based on previous work which had shown the importance of protozoans in marine ecosystems, and their role in ingesting particles in the 0.2 to 2 micron size class range - an important reservoir of particulate metals and contaminants in seawater. We anticipated that the grazing process would create a chemical microenvironment where many processes would be accelerated relative to bulk seawater.

This project was an AASERT Award and was the dissertation research of Katherine A. Barbeau, MIT/WHOI Joint Program.

# Approach

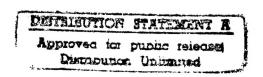
The approach was to changes in the particle size spectrum and chemistry of metals associated with bacteria and also colloidal minerals (e.g. ferrihydrite) associated with bacterial size particles. The latter was used as a probe of low pH environments, since it is relatively hard to dissolve at seawater pH (8), but dissolves rapidly at lower pH values encountered in protozoan vacuoles (2-3). Ferrihydrite was impregnated with an inert tracer, Ba-133, which enabled us to calculate forward rates of colloid dissolution even when the Fe was taken up on some other phase. The Ba-133 also served as a model for how a contaminant associated with a metal oxide colloid could be released through the grazing process. Changes in colloid surface chemistry after grazing and egestion were also followed using electrochemical and ligand competition methods.

Transformations of bacterial associated metals were followed primarily by monitoring changes in particle size distributions for each metal during grazing.

#### Results

We have shown that protozoan grazing influences metal chemistry in the following ways

• Dramatically altering the particle size spectrum, moving metals into very small (i.e. colloidal) particles and also into large aggregates. Relatively particle reactive metals such as Fe(III), Cr(III) and Th(IV) can be transformed into "dissolved" forms which are actually colloids produced by the protists.



• Dissolving minerals such as ferrihydrite, increasing the reactivity of particulate Fe and its biological availability. Field experiments indicate that protozoan grazing is the predominant pathway for colloidal Fe dissolution in coastal waters, an important finding given that Fe is abundant in coastal waters but is almost entirely particulate. Protozoans may play an important role in cycling this iron and maintaining a biologically available stock. We demonstrated this by showing that protozoans could render colloidal Fe available to Fe limited diatoms.

## Significance

Protozoans can increase metal mobility by dissolving refractory minerals and by associating particle reactive metals like Cr(III) with colloids. This has important implications for metal geochemistry in the open ocean, where the protozoan mediated "microbial loop" often predominates, and also in coastal environments where a dense protozoan population can enhance the mobility of contaminants. Our work shows that a whole new class of microenvironment-mediated processes must be considered when studying the chemical fate of trace metals and contaminants.

#### Naval Relevance

Our results are highly relevant to bioremediation process studies, because bioreactors generally have huge protozoan populations. Modifications to contaminant reactivity and bioavailability mediated by protozoans may become an important consideration in determining the efficiency or side effects of a specific bioremediation process.

### **Publications**

Barbeau, K.A., Mofett, James W. Caron, D.A. Croot, P.L. and Erdner, D.L. (1996) Role of protozoan grazing in relieving Fe limitation of phytoplankton. *Nature* 380 61-64.